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INFLUENCE OF EXPOSED AREA ON STRESS-CORROSION CRACKING
OF 24S ALUMINUM ALLOY

By William H. Colner and Howard T. Francis

Armour Research Foundation



Washington

November 1954

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INFLUENCE OF EXPOSED AREA ON STRESS-CORROSION CRACKING
OF 24S ALUMINUM ALLOY

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SUMMARY

Results are reported of a study of the "area effect" in 24S aluminum alloy. By area effect is meant the phenomenon whereby small areas show long times to failure while large areas show short times. The effects of stress level, degree of sensitivity of the alloy, and hydrogen peroxide concentration in the corrosion medium were studied. Substitution of oxygen for hydrogen peroxide also was investigated.

In addition to the principal result (the determination of area versus time to failure) the data show that stress levels above 60 percent of the yield strength of the alloy are uniformly effective in producing stress-corrosion failure. The area effect seemed most pronounced with specimens having maximum sensitization (quenched and aged 6 hours at 325° to 375° F). Hydrogen peroxide was found to decompose very rapidly in the presence of corroding 24S alloy; the decomposition was due to the cupric ion produced during the corrosion. The stress corrosion of 24S was found to be very sensitive to hydrogen peroxide concentration in the range 1.5 to 3.5 grams per liter. Oxygen was ineffective in promoting stress-corrosion cracking when substituted for peroxide.

INTRODUCTION

As a part of a broad study of the stress-corrosion cracking of aircraft alloys, attention has been given to the mechanism involved in the failure of 24S aluminum alloy. This report presents the results of a study of the "area effect." This effect is of considerable importance in arriving at a satisfactory general explanation for the stress-corrosion phenomenon. The effect has been observed in magnesium-base alloys (ref. 1) but has not been studied extensively for aluminum-base alloys.

The area effect can best be defined qualitatively as the phenomenon whereby small exposed areas do not suffer stress-corrosion failure in nearly so short a time as do large areas. This effect was explained for magnesium alloys on an electrochemical basis, as follows: When a small area of corroding surface is exposed, there is insufficient cathodic

activity to permit the anodic action (cracking) to proceed. This theory is reasonable, since the corrosion process is known to be under cathodic control. It is further substantiated by the fact that a small-area specimen (too small to crack when exposed alone to the corrosion medium) will crack readily if the specimen is electrically coupled to a large auxiliary specimen of the same alloy. Furthermore, current measurements between the two specimens showed that anodic action on the small (stressed) specimen was greatly increased by coupling to the large (unstressed) auxiliary specimen.

The present work on 24S aluminum alloy had as its major objective to ascertain definitely whether or not the area effect exists in this alloy and, if possible, to find the explanation for it. Many unforeseen complications arose, which led to studies of hydrogen peroxide decomposition, the effect of substituting oxygen for peroxide, and the influence of peroxide concentration on the area effect. Also studied were the effect of degree of sensitivity on the area effect and the effect of stress level on the area effect.

This work was conducted at Armour Research Foundation under the sponsorship and with the financial assistance of the National Advisory Committee for Aeronautics.

EXPERIMENTAL WORK

Materials

With one exception all experiments were performed on 24S aluminum alloy, obtained commercially as rolled sheet. In the experiment on the effect of stress level, a high-purity binary alloy of 4 percent copper in aluminum was used, obtained through the cooperation of the Research Laboratories of the Aluminum Company of America.

The chemicals used in the preparation of the corrosion mediums were chemically pure or equivalent. The stock hydrogen peroxide was 30 percent H_2O_2 , unstabilized.

Test Apparatus

The stress-corrosion experiments were performed using two-specimen stress jigs, one of which is shown in figure 1. It employs four-point loading of a strip specimen. The stress was applied by placing appropriately weighted containers (of mercury) on each platform of the stress jig.

After the load was applied, a microswitch (under the platform) was adjusted so that a further deflection of the specimen (caused by cracking) would interrupt a running time meter. The precise value of this additional deflection could be selected at will by means of a screw adjustment (visible in fig. 1).

Figure 2 shows the assembly of 10 double units, together with the running time meters and the storage vessel for the corrosion medium. In this arrangement the solution was circulated continuously through the system by means of a small centrifugal pump (not visible).

In some runs (where peroxide level was a variable), individual containers were used for each pair of test specimens; in others, all stress jigs were placed in the large container shown in figure 2.

In all cases in which specimens were partially stopped off (to limit the exposed area) a standard plating stop-off lacquer was used.

RESULTS

Effect of Stress Level

The experiment to be described was performed before the importance of peroxide concentration was fully realized and before certain refinements were made in the stress jigs used. The results indicate the effect of stress level, however, and are therefore included.

Specimens were prepared from high-purity aluminum-base alloy containing 4 percent copper and were stopped off to expose two extremes in area. The "small" areas were 0.1 by 1.9 centimeters while the "large" areas were 8.5 by 1.9 centimeters. Ten specimens were run for each area value.

The solution used was 53 grams per liter of sodium chloride NaCl containing 3 grams per liter of H_2O_2 . It was changed daily in an attempt to maintain a constant peroxide level. (Later data indicated that this replacement schedule was not frequent enough.)

Several stress levels were used and the time to failure was recorded for each specimen. The results are shown in figure 3.

It will be seen that the reproducibility of the data is not so good as would be desired. The effect of stress is sufficiently clear, however, to indicate that levels above 60 percent of the yield strength produce essentially the same time to failure (for a given exposed area).

Similarly, the small-area specimens show a significantly longer time to failure than the corresponding large-area specimens. It might also be noted that the large-area specimens show somewhat better reproducibility than do the small-area specimens.

Effect of Aging Temperature

For the determination of the effect of aging temperature and all further experiments, 24S alloy was used in place of the high-purity binary of 4 percent copper in aluminum. Accordingly, it was considered desirable to determine the aging and sensitization characteristics of the 24S alloy.

In this experiment, specimens were prepared at various aging temperatures and exposed to the usual $\text{NaCl} + \text{H}_2\text{O}_2$ medium, using the apparatus already described. The physical properties of the specimens, together with their times to failure, are shown in figure 4. The solid- and open-circle points represent the results of two separate experiments. The runs marked with crosses were accidentally interrupted after 18 hours; when the specimens were reexposed, many of them would not support the load.

Although reproducibility is not good, it appears that maximum susceptibility to stress-corrosion failure is obtained in the range of 325° to 375° F, using a treatment time of 6 hours.

It is felt that the poor reproducibility is in part due to hydrogen peroxide decomposition, which was studied subsequently (see below).

In an attempt to determine the effect of susceptibility on the area effect, a further experiment was run, employing large and small areas, each heat treated at two temperatures (310° F and 350° F) for 6 hours. The time to failure was noted for five specimens of each of these four types.

The results are shown in table I, together with pertinent experimental details. Unfortunately, most of the small-area specimens had not failed when the test was discontinued. It seems quite likely, however, that the area effect would be most pronounced with the specimens aged at 350° F, since the large specimens treated at this temperature failed in 1.2 hours (average). The specimens aged at 310° F, on the other hand, showed much less spread between the two areas.

Substitution of Oxygen for Hydrogen Peroxide

It was discovered during the course of the experiments just described that the H_2O_2 in the corrosion medium suffered quite rapid decomposition

(even using the arrangement shown in fig. 2). Accordingly, an attempt was made to use oxygen (O_2 gas) instead of H_2O_2 in the medium.

The experiment described in the section "Effect of Aging Temperature" was repeated, using the same strength of NaCl (53 grams per liter) but substituting oxygen for H_2O_2 . The oxygen was passed into each bath (holding two specimens) through a gas disperser. The rates were sufficiently high to assure virtual saturation in each container.

No failures occurred in 337 hours (14 days) for either large or small areas. Thus it was conclusively shown that the role of hydrogen peroxide is not simply to furnish oxygen to the bath by decomposition.

Further work, therefore, again employed H_2O_2 but with much closer attention given to maintenance of its concentration.

Hydrogen Peroxide Decomposition

In order to obtain some basic information on the causes for and rates of decomposition of H_2O_2 in the corrosion medium, a series of gas-evolution tests was run on NaCl- H_2O_2 solutions. The cell used is shown in figure 5 and is the type normally used for measurement of hydrogen evolution during metal corrosion. The evolved gas (O_2 in this case) collects in the top of the cell proper, thus displacing solution into the burette above.

The standard solution of 53 grams per liter of NaCl containing 3 grams per liter of H_2O_2 was used in all tests. For standardization, the cell was filled with solution alone and warmed to decompose the peroxide, and the total oxygen content was determined. Thus, 300 cubic centimeters of solution yielded 319 cubic centimeters of O_2 gas.

The influence of various metal specimens was then determined, with the results shown in figure 6. It is seen that 24S alloy promotes H_2O_2 decomposition, roughly in proportion to the area of the specimen. Pure aluminum, on the other hand, has no effect. Since the major difference between pure aluminum and 24S is the copper contained in the latter, a further test was run as follows:

After the test with pure aluminum had run for 5 hours, a small piece of metallic copper was added to the test cell. The rate immediately increased to about 8 cubic centimeters per hour. Similarly, after the "solution only" test had run for 5 hours, a few crystals of cupric chloride were added to the cell; the rate jumped to 300 cubic centimeters per hour, establishing the fact that cupric ion was the effective catalyst in promoting peroxide decomposition. This role of Cu^{++} was confirmed in the inorganic literature.

It is interesting to note that the above results indicate that appreciable concentrations of copper ion enter the solution during the corrosion of 24S alloy.

Effect of H_2O_2 Concentration on Stress Corrosion

In view of the instability of peroxide under the conditions required in the testing of 24S alloy, it seemed desirable to relate the time to failure for sensitized 24S specimens with the peroxide concentration. Accordingly, a number of duplicate 24S specimens were quenched and aged at $350^\circ F$ for 6 hours. They were exposed to the corrosion medium (53 grams per liter of NaCl) at an applied stress of 80 percent of the yield strength. Various H_2O_2 concentrations were used, with the results shown in figure 7.

It is seen that the time to failure is very sensitive to H_2O_2 concentration. It is now clear that in order to obtain reproducible data on time to failure, rather closer control is required than was employed in earlier work.

It was noted during the above tests that the nature of the attack on the 24S specimens varied quite markedly as the peroxide concentration was increased. Three selected specimens from the data of figure 7 were examined metallographically. They correspond to 1.5, 1.8, and 3.5 grams per liter of H_2O_2 in the corrosion medium and are shown in figures 8, 9, and 10.

The photomicrographs show that only slight intergranular penetration occurs at 1.5 grams per liter, while much more is evident at 1.8 grams per liter and still more at 3.5 grams per liter. It is evident that the penetrative nature of the salt-peroxide corrodent is very closely related to the hydrogen peroxide concentration.

It will not be attempted to develop an explanation for the critical role of hydrogen peroxide in the cracking mechanism; rather, it will suffice to point out that very close experimental control of the H_2O_2 concentration must be exercised if the time-to-failure data are to be significant.

Area Versus Time to Failure

In view of the data presented above, it can now be understood why preliminary experiments on the area effect were not conclusive. Taking into account the several factors studied above (the most important of which is the peroxide content of the corrosion medium), the determination of the relation between area and time to failure was again attempted.

In order to confirm the rather marked effect of peroxide concentration and at the same time to get preliminary area-effect data, the following experiment was performed:

Large- and small-area specimens of sensitized 24S alloy were prepared as before. Five peroxide concentrations were selected, ranging from 1.5 to 3.5 grams per liter. Specimens of each area were exposed to each of the five peroxide levels. The results and experimental conditions are shown in figure 11.

The reproducibility and consistency of the data are rather striking compared with earlier results. At 3.5 grams per liter very little difference in time to failure is found between the large- and small-area specimens. At approximately 2 grams per liter, however, the difference is quite marked. At very low levels it is difficult to say whether or not an area effect exists, since the times to failure are quite long even for large areas.

Based on the results of figure 11, a second experiment was run, in which the peroxide concentration was held constant at 2.5 grams per liter. Several different areas were studied, ranging from 0.1 centimeter by 1.9 centimeters to 7.0 by 1.9 centimeters. The results and experimental conditions are shown in figure 12 (open circles).

In order to establish that the differences in time to failure were due to area only, a further experiment was run in which the same types of specimens were exposed, except that each was coupled to an auxiliary specimen of the same alloy (unstressed). The areas of the auxiliary electrodes were so selected that the total metal area exposed was the same for all specimens (7.0 by 1.9 centimeters).

The results of this experiment are also shown in figure 12 (solid circles). There can be little doubt that the difference between the two curves is due to electrochemical causes rather than mechanical ones, since all conditions were identical in both runs except the area exposed.

DISCUSSION

It has been shown that, when 24S aluminum alloy is sensitized to stress-corrosion cracking, the time to failure is dependent on the area of the corroding surface. The area effect is very much influenced by the hydrogen peroxide concentration in the corrosion medium. The stress level and degree of sensitization are not nearly so critical.

At high H_2O_2 levels there is relatively little difference in time to failure for small and large areas; at lower peroxide levels, however,

the difference is marked - the smaller areas requiring much longer times for failure.

These facts point to the conclusion that the role of H_2O_2 is that of a cathodic depolarizer. Furthermore, at a given peroxide concentration, sufficient total specimen area must be available to permit a certain amount of cathodic action - which, in turn, is sufficient to support the actual anodic action (cracking) at the grain-boundary zones.

It should be pointed out that this result is in direct support of the Dix theory for stress-corrosion cracking of this alloy, at least insofar as the beginning of the cracking process is concerned. There is, of course, the possibility that, as cracking proceeds, the cathodic function of the peroxide-depolarized grain-center regions may be supplanted by cathodic action within the crack itself. That is, as the metal begins to rupture, the freshly exposed (and highly reactive) metal at the crack apex may be sufficiently anodic to force hydrogen evolution to occur. Under these conditions, one would expect the hydrogen to be evolved very close to or even within the crack itself.

As a matter of fact, the evolution of hydrogen from within a progressing crack has been observed in both magnesium-base alloys and aluminum-base alloys (ref. 2).

Although no attempt will be made to explain it, an interesting result of the present work is the demonstration that oxygen is not at all equivalent to hydrogen peroxide in promoting the stress-corrosion cracking of 24S alloy. Since a sintered-glass gas disperser was used in the oxygen experiments, there can be little doubt that the corrosion medium was saturated with oxygen (or very nearly so).

CONCLUSIONS

The following conclusions have been drawn from the results of a study of the area effects in 24S aluminum alloy:

1. The 24S aluminum alloy exhibits an area effect which is quite critically dependent on the hydrogen peroxide concentration. Under the conditions of the experiments, the maximum area effect was noted at about 2.0 grams per liter of hydrogen peroxide, but this value is dependent on several variables, mainly agitation and temperature. A stress level in excess of about 60 percent of the yield strength does not appreciably influence the area effect. The degree of sensitization affects the area effect, though not so markedly as the peroxide concentration, and the maximum area effect was observed at maximum sensitization (quenched and aged at 350° F for 6 hours).

2. The area effect in 24S alloy is shown to be an electrochemical phenomenon and not a mechanical one.

3. The rapid failure of 24S in the corrosion medium (sodium chloride containing hydrogen peroxide) is not noted when oxygen is substituted for the peroxide.

4. Hydrogen peroxide decomposes rapidly when used in the corrosion medium for the exposure of copper-bearing aluminum alloys, since the cupric ion, a corrosion product of the alloy, is a catalyst for this decomposition. Furthermore, it is observed that time to failure is sensitive to the hydrogen peroxide concentration (especially between 1.5 to 3.5 grams per liter). It is, therefore, important that the peroxide level be maintained as closely as possible. Since close adherence to the nominal peroxide level is required and since peroxide is catalytically decomposed by a corrosion product, it is necessary that frequent peroxide determinations and additions be made during the course of any exposure tests.

Armour Research Foundation,
Chicago, Ill., September 4, 1953.

REFERENCES

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2. Edeleanu, C.: A Mechanism of Stress Corrosion in Aluminum-Magnesium Alloys. The Jour. Inst. Metals, vol. 80, pt. 4, Dec. 1951, pp. 187-191.

TABLE I

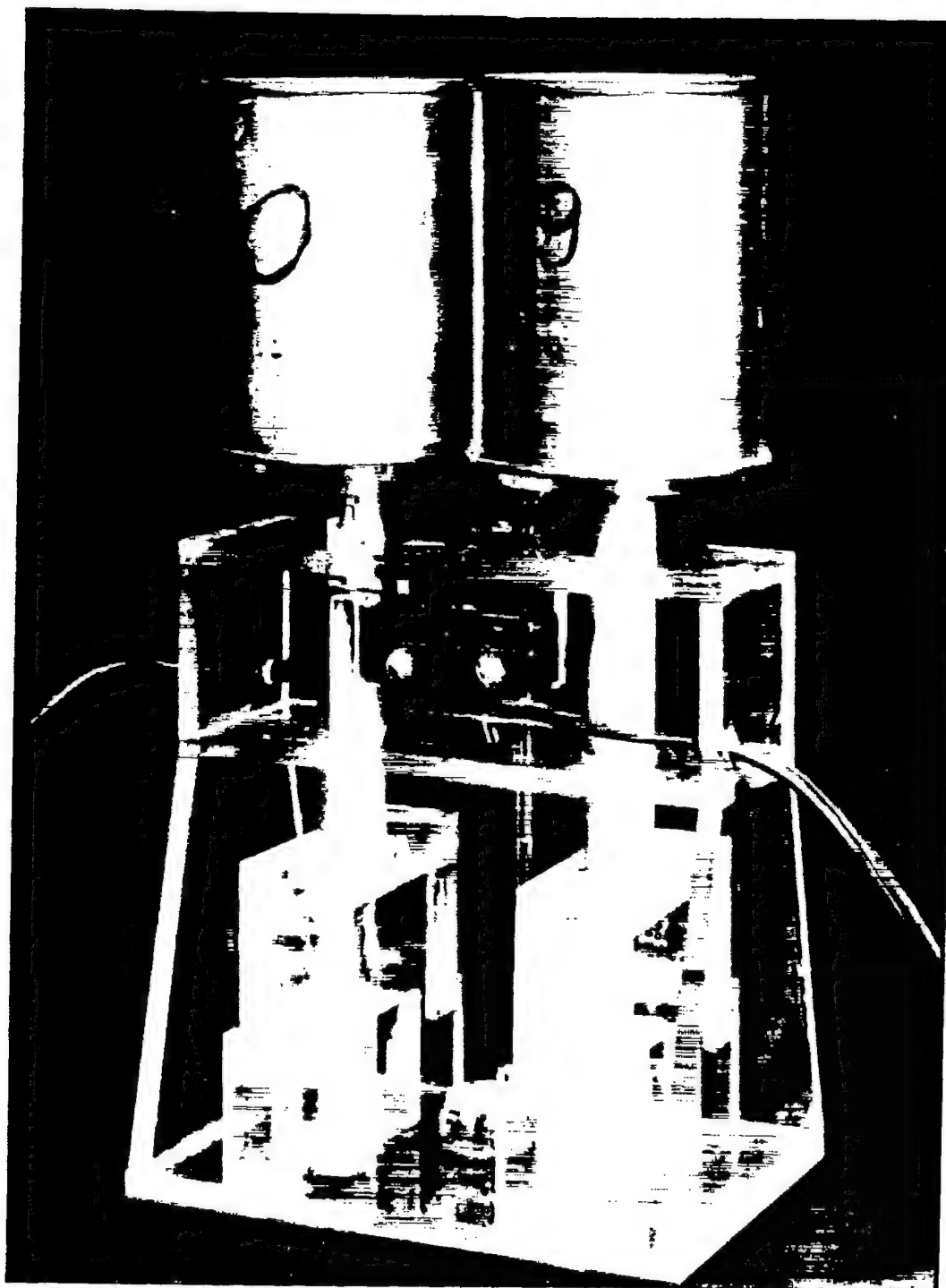
INFLUENCE OF DEGREE OF SENSITIVITY ON AREA EFFECT

[Corroding medium: 53 g/l NaCl + 3 g/l H₂O₂, using 16 gal of solution]

Temperature of aging, °F (a)	Exposed area, cm	Specimen	Time to failure, hr (b)
310	7.0 by 1.9	A-501	3.2
		A-502	22.6
		A-503	39.6
		A-504	11.4
		A-505	<u>22.6</u>
		Av.	19.9
	.1 by 1.9	B-506	45.8+
		B-507	12.0
		B-508	45.8+
		B-509	45.8+
		B-510	45.8+
350	7.0 by 1.9	C-511	1.2
		C-512	1.9
		C-513	1.1
		C-514	1.1
		C-515	<u>.9</u>
		Av.	1.2
	.1 by 1.9	D-516	42.0
		D-517	45.8+
		D-518	45.8+
		D-519	45.8+
		D-520	45.8+

^aSpecimens were aged at indicated temperature for 6 hr.

^bTest was discontinued at 45.8 hr; specimens showing this time had not yet failed.



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Figure 1.- Stress-corrosion fixture after alterations.



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Figure 2.- Stress-corrosion setup using single tank and reservoir.

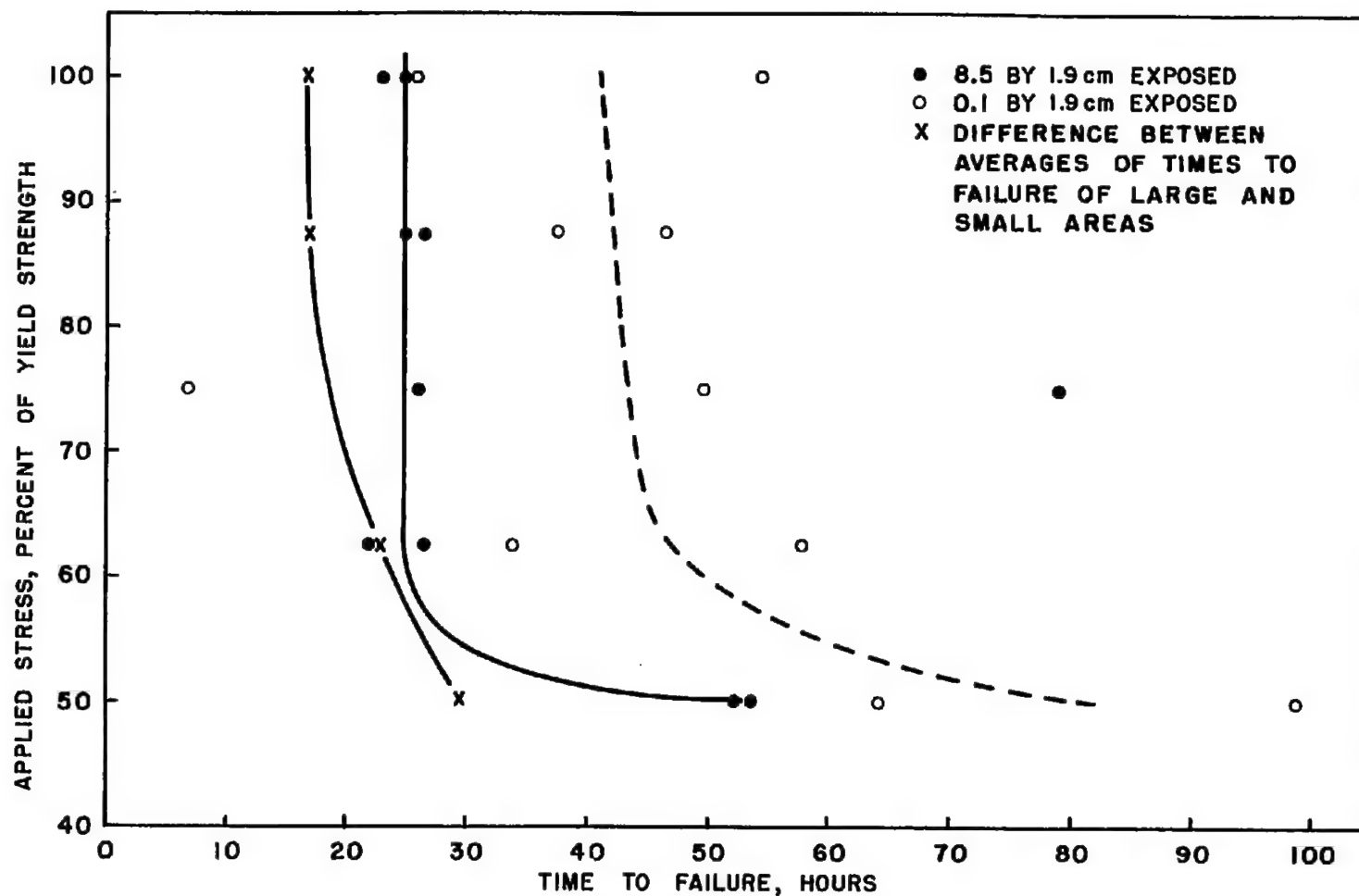


Figure 3.- Time to failure of 4-percent copper - aluminum-base alloy as function of applied stress. Specimens quenched from 910° to 930° F and aged for 8 hours at 390° F. Corrosion medium, 53 grams per liter of sodium chloride plus 3 grams per liter of hydrogen peroxide.

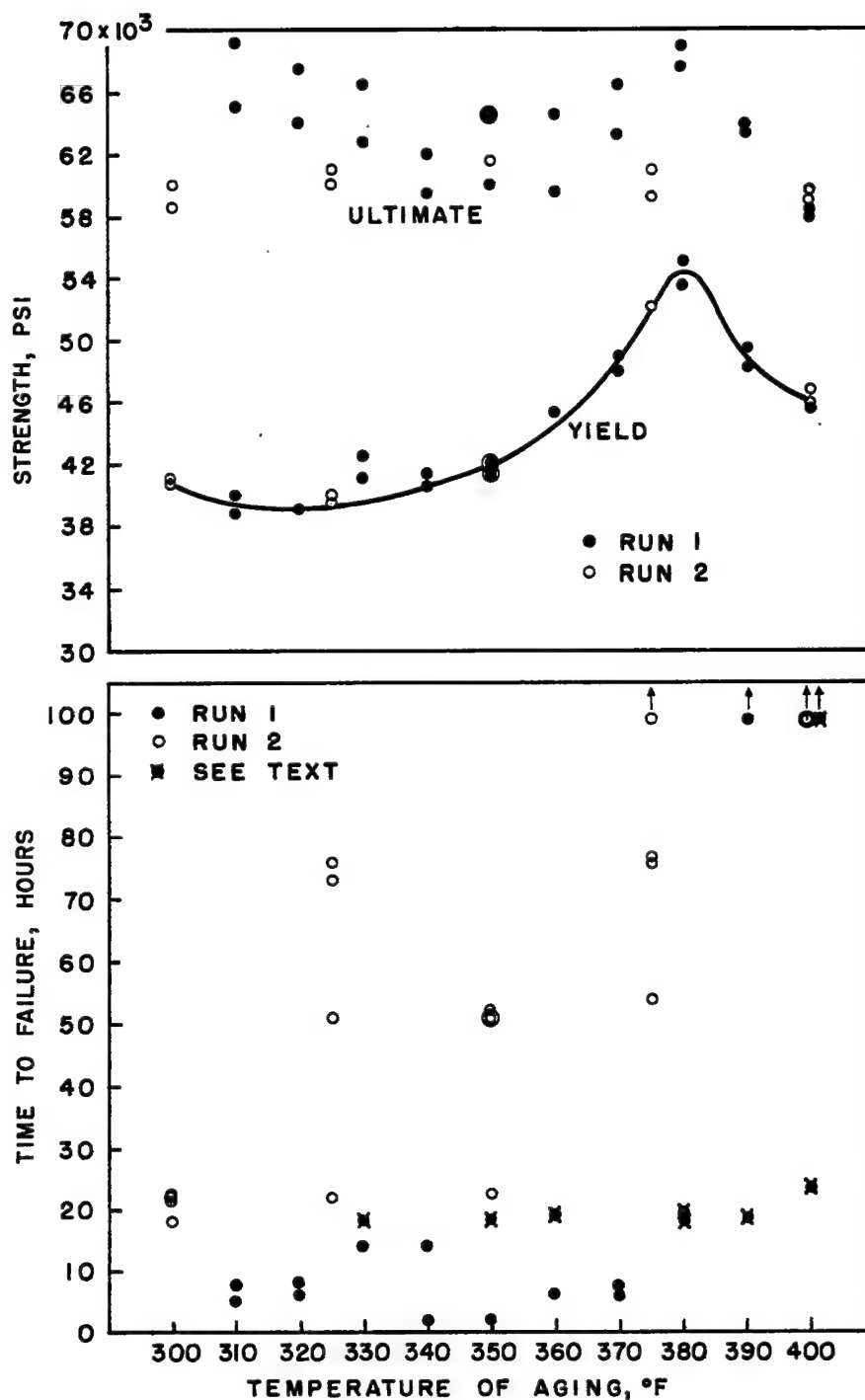


Figure 4.- Mechanical properties and time to failure of 24S specimens quenched from 910° to 930° F into cold water followed by aging for 6 hours at indicated temperatures. Corrodent, sodium chloride plus hydrogen peroxide.

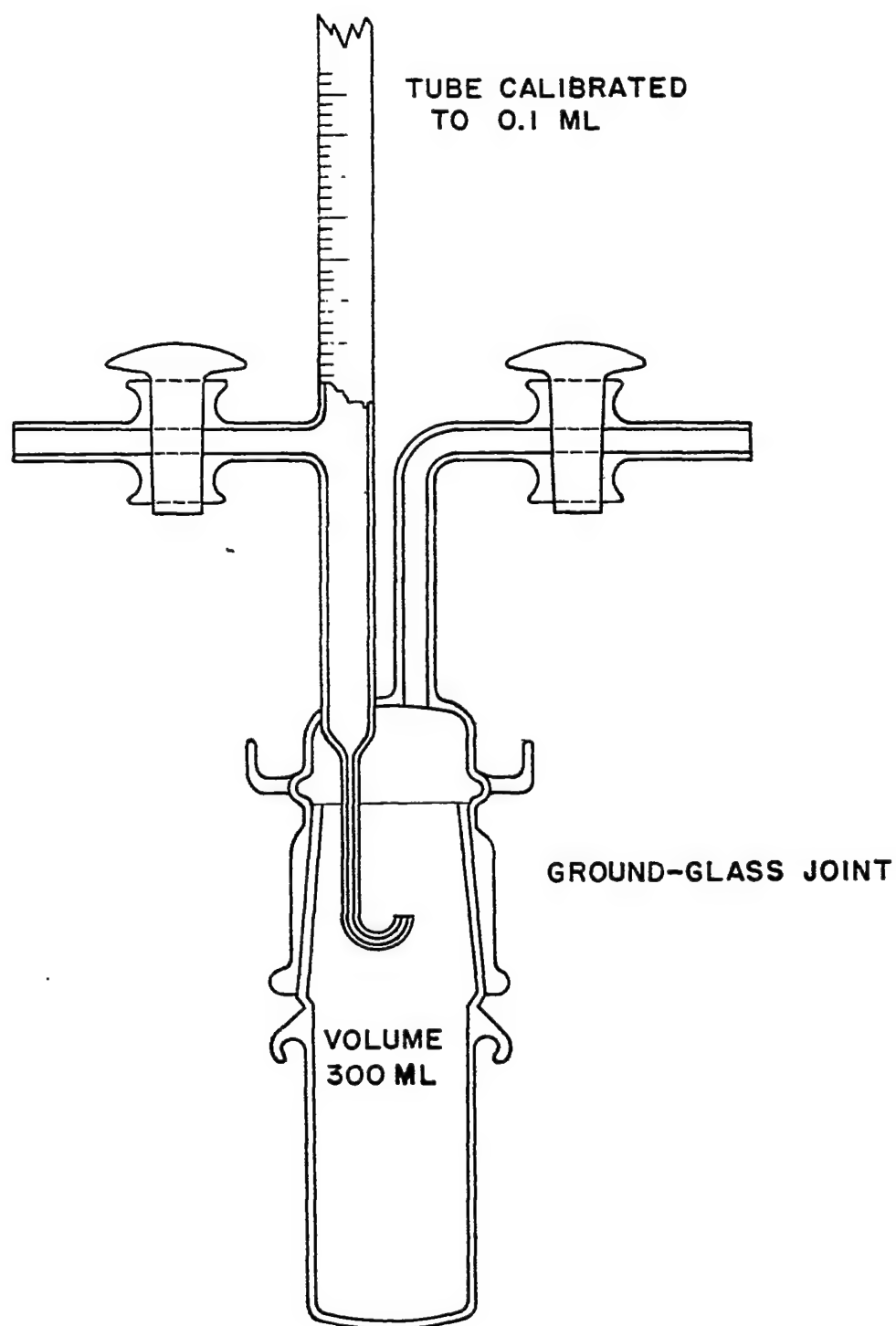


Figure 5.- Gas-measuring cell.

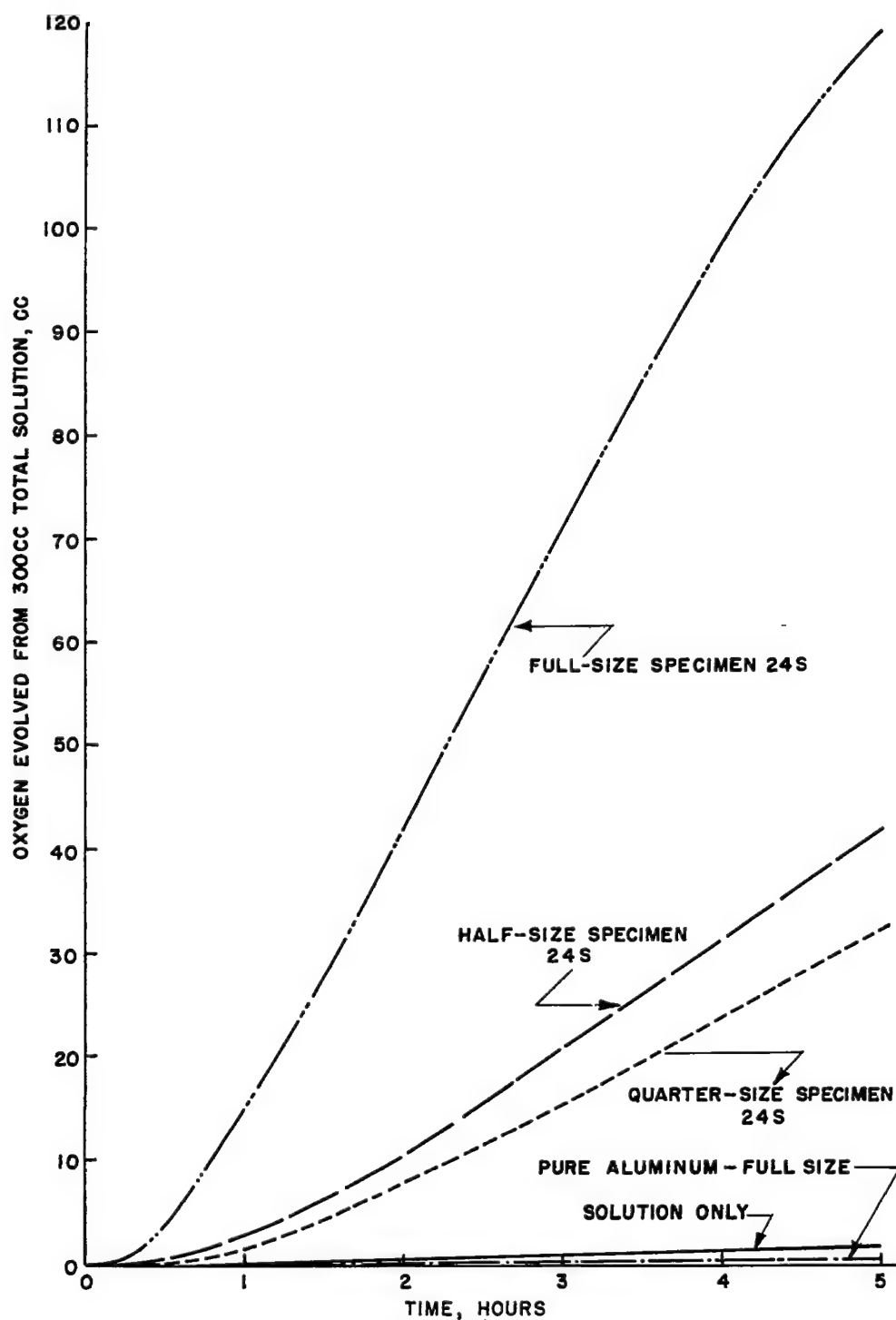


Figure 6.- Effect of amount of exposed area and alloy on decomposition of hydrogen peroxide. Solution, 53 grams per liter of sodium chloride plus 3 grams per liter of hydrogen peroxide; total volume of oxygen in solution, 319 cubic centimeters per 300 cubic centimeters of solution.

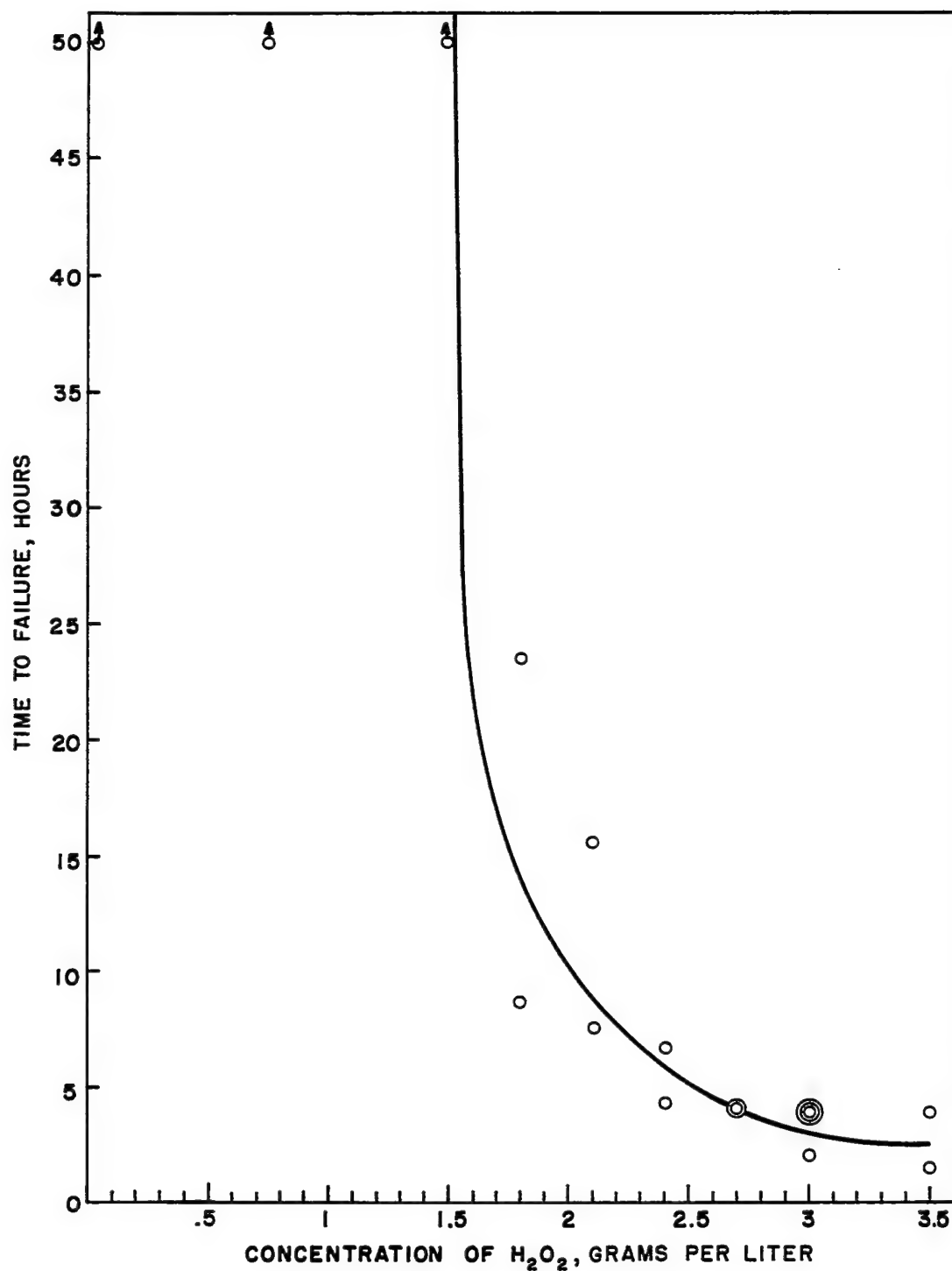
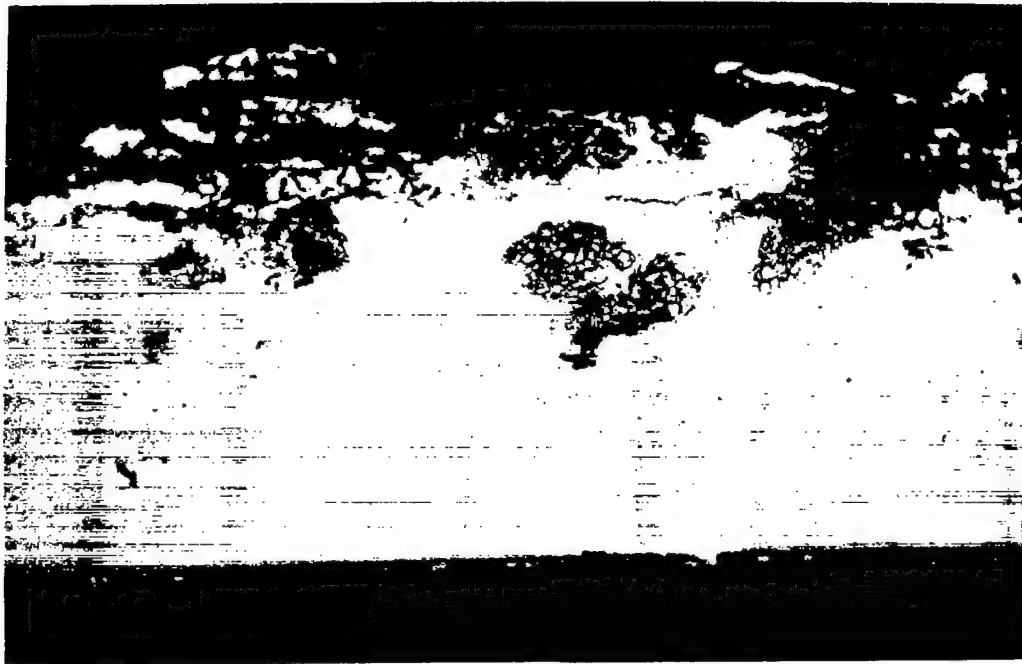
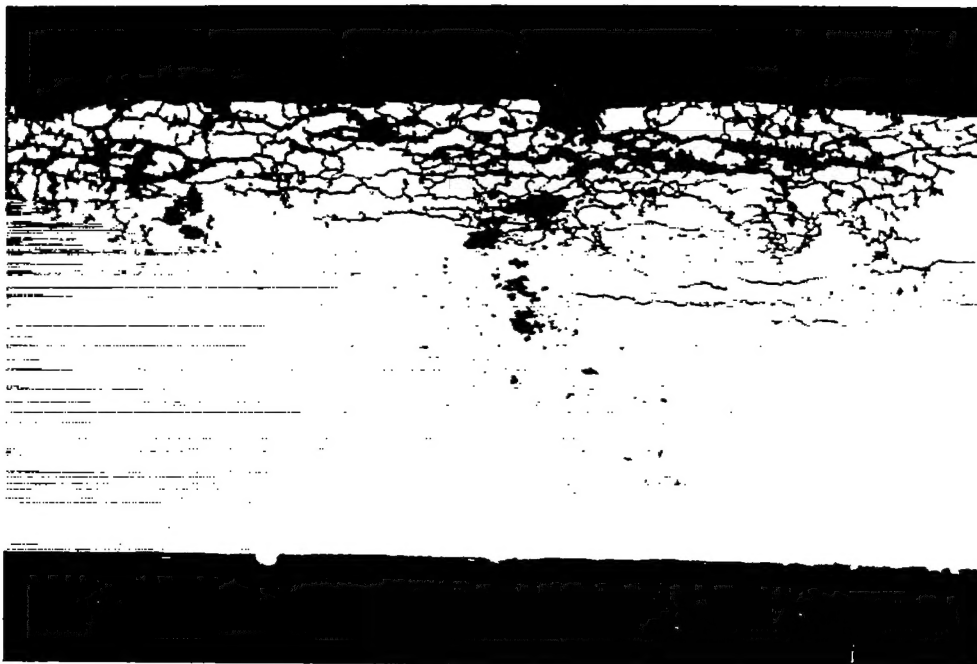


Figure 7.- Effect of hydrogen peroxide concentration on time to failure in 53 grams per liter of sodium chloride. Specimens were 24S alloy stressed to 80 percent of the yield strength; quenched and aged at 350° F for 6 hours.



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Figure 8.- Photomicrograph of sensitized 24S specimen after exposure to 53 grams per liter of sodium chloride plus 1.5 grams per liter of hydrogen peroxide for 50 hours. Failure had not occurred; unetched; 75X.



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Figure 9.- Photomicrograph of sensitized 24S specimen after exposure to 53 grams per liter of sodium chloride plus 1.8 grams per liter of hydrogen peroxide for 8.7 hours, at which time failure occurred. Unetched; 75X.



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Figure 10.- Photomicrograph of sensitized 24S specimen after exposure to 53 grams per liter of sodium chloride plus 3.5 grams per liter of hydrogen peroxide for 1.6 hours, at which time failure occurred. Unetched; 75X.

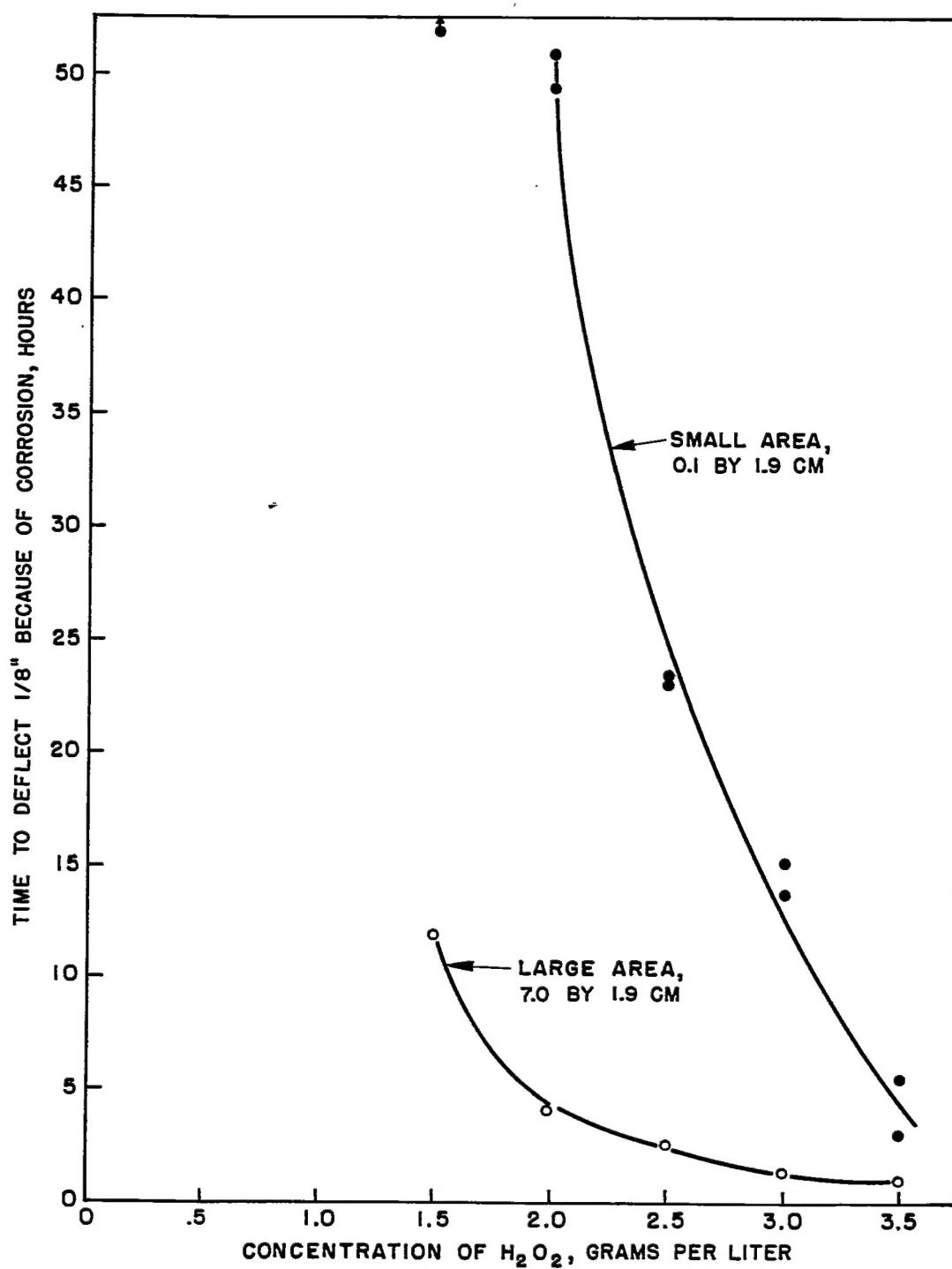


Figure 11.- Influence of peroxide concentration on area effect. 24S alloy sensitized; solution, 53 grams per liter of sodium chloride plus hydrogen peroxide; applied stress, 80 percent of yield strength.

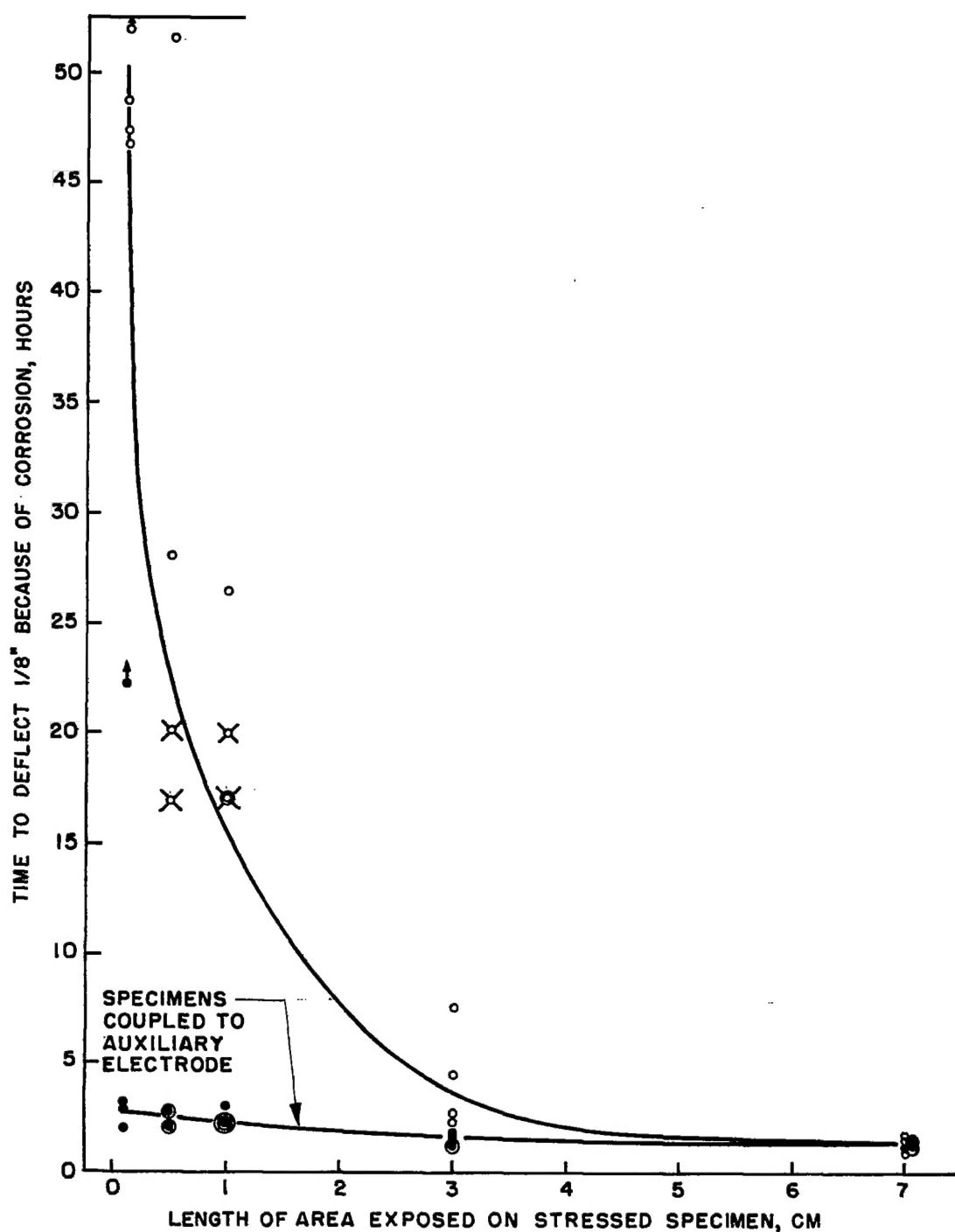


Figure 12.- Area effect for 24S alloy and influence of an auxiliary electrode. Width of exposed area, 1.9 centimeters; 24S alloy sensitized; solution, 53 grams per liter of sodium chloride plus 2.5 grams per liter of hydrogen peroxide; applied stress, 80 per cent of yield strength.